

9th Eco-Energy and Materials Science and Engineering Symposium

Preparation of Knitting Socks from Poly (lactic acid) and Poly [(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] (PHBV) blends for Textile Industrials

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Abstract

The PLA/PHBV blends were prepared using dry blend in the melt spinning method. The ratios of PLA:PHBV were varied with 100:0, 95:5, 90:10, 85:15 and 80:20 wt%. The temperature of single screw extruder was set at 210 to 235°C with screw speed 9 rpm and free fall at draw speed 450, 500 and 550 m/min. The textile fibers were subjected to thermal, morphology and mechanical property evaluation. The results show that the addition of PHBV was compatible with PLA in the textile fibers and increased the flexibility of the blends. The ratios of PLA/PHBV at 95/5 and 90/10 was used for the preparation of knitting socks. The Sonic velocity and Tenacity of the fiber was found to be 2.37% and 0.93 CN/den, respectively.

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Selection and/or peer-review under responsibility of CEO of Sustainable Energy System,

Rajamangala University of Technology Thanyaburi (RMUTT).

Keywords: Biodegradable plastics; melt spinning; poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] (PHBV); polymer blends; poly(lactic acid)

1. Introduction

Research and investigation have been focus on discover and development of new fibers that are friendly to environment. These phenomena are arisen from the limitation of non-degradable fibers synthesized from petroleum products. The amount of textile materials consumed has been increasing drastically due to the numbers of population. Wastes of those textile products have been increasing as they need more than a hundred years to be degraded. Therefore, the application of biodegradable polymers to textile industry is an important issue for the alternative ways to solve the environmental problems. Biodegradable fibers studied and produced are made from polyesters such as poly(lactic acid) (PLA) or polylactide, a linear thermoplastic polyester synthesized from biomass [1].

PLA is synthesized by a direct polycondensation of lactic acid or by a ring-opening polymerization of lactide. Lactic acid and lactide exhibit two stereoisomer structures, D- and L-isomers, which results to two

structures of polymer synthesized, PDLA and PLLA [2,3]. The polymer molecules contain mixture of both isomers are called racemic PLA, PDLLA or PLA, shows lower thermal and mechanical properties than the pure isomers but it is more economically susceptible.. PLA is one of the most promising biodegradable polymers available commercially. However, PLA exhibits stiff and brittle behaviour which made it difficult to be used in fabrication process for industrial applications. The low impact toughness and elongation at break have been limiting factors to diversification in applications of PLA [4-5]. We have studied the preparation of polymer blends of PLA and other biodegradable polymers to increase the toughness and flexibility of PLA. Poly(3-hydroxybutyrate) (PHB) is a fully biodegradable polyester with optical activity, piezoelectricity, and very good barrier properties. The blending of PLA and PHB exhibits better results of mechanical property which can be applied to packaging applications. However, the polymer blends of PLA and PHB still show limitation to apply for textile products on elongation and fabrication processes.

Sarun *et al.*, reported the preparation method of polymer blends between PDLLA and (Poly[(R)-3-hydroxybutyrate-co-(R)-3-hydroxyvalerate] (PHBV) and fabricated to fibers [4]. The addition of polyethylene glycol (PEG) in a polymer blend allows interfacial between the PDLLA with PHBV. The fibers showed higher percentage of elongation at break, But the tensile strength decreases with increasing the amount of PHBV. PHBV is biodegradable polymer, biological family of poly(hydroxy alkanate) (PHA) consists of the poly-3-hydroxybutyric acid (PHB) and poly-3-hydroxyvaleric acid (PHV). The PHB and PHV derived from fermentation of glucose acid and propionic acid with low T_m and T_g from 143 to -4°C , so it is flexible and can be easily produced [5-6]. PHBV can be used in the production process, such as bottles and film, biodegradable clothing composite membrane used for separation process and medical devices.

In this research we had studied the preparation of polymer blends of PLA and PHBV with the aims to apply for fiber applications. The mechanical and thermal properties of the blends were studied. The biodegradable fibers were applied to textile fabrications.

2. Experimental

2.1. Materials

The commercial PLA (Natureworks PLA 3001D injection molding grade) in pellet form exhibits a density of 1.24 g/cm^3 , melt flow rate (MFR) of 22 g/10min , tensile strength of 62 MPa , elongation at break of 3.5% and impact strength of 16 J/m . Poly(R)-3-hydroxybutyrate-co-R-3-hydroxyvalerate] (PHBV) (Y1010P) was purchased from purchase from ENMAT co., Ltd. in pellet form. PHBV exhibits a modulus of 900 MPa , elongation at break of 15% , glass transition temperature and melting point of 5 and 150°C , respectively.

2.2. Preparation of PLA and PHBV fiber blends using melt spinning technique

The pellet of both PLA and PHBV were initially dried in a vacuum oven at 80°C for 12 hours to remove moisture before processing through the twin-screw extruder. Blends of PLA and PHBV with various compositions 100/0, 95/5, 90/10, 85/15 and 80/20 wt% were mixed by Fourné Modular melt spinning machine from hopper to dies at 210 to 230°C for 10 minutes with a rotate speed of 80 rpm .

2.3. Thermal properties

The differential scanning calorimetry (DSC) was used to evaluate the thermal properties of the PLA/PHBV blends. The testing was carried out on a Perkin elmer DSC 8000. The thermogram signal was derived from the temperature difference between the sample and the reference. The sample of $5\text{-}10\text{ mg}$ was placed in a crimped aluminium pan. The DSC of PLA/PHBV blends were carried out under N_2 atmosphere at heating rate at a constant 10°C/min and heated to 200°C . The melting temperature (T_m)

and glass transition temperature (T_g) were calculated from the midpoint of the base-line shift of the DSC thermogram.

2.4. Mechanical properties

The tensile tests to determine the tensile strength and elongation at break of the blend were done using a model LLOYD Instrument universal testing machine according to SD - QA – 002. The specimens were strained at a rate of 0.83 mm/s at room temperature. The report value was the average of three replicates for each property test.

2.5. Scanning electron microscopy (SEM)

The morphology of the fracture surface of the PLA/PBSA/PBAT blends was investigated using a JEOL model JSM-6400 scanning electron microscope at 10 kV. The specimens were fractured under cryogenic condition using liquid nitrogen. Then, the specimens were mounted on a SEM stub using a double-side tape and the fracture surface of specimens was sputtered with a thin gold layer.

3. Results and Discussion

3.1. Molecular weight

Table 1 shows molecular weight analysis of fibers of PLA and PLA/PHBV blends. The pure PLA has MW of 65180 g/mol and after preparation of PLA fibers the MW decreased to 36330 g/mol. The results revealed degradation of polymer chain through the fabrication processing. The polymer blends showed decreased of molecular weight of PLA after processing slightly lower than the pure polymer. The optimized ratios of PLA/PHBV for fiber preparation are 95:5 and 90:10 wt%.

Table 1. Molecular weight of PLA/PHBV fibers.

Ratio of PLA/PHBV (wt%)	Molecular weight (g/mol)
PLA chip	65180
PLA Free fall	36330
95/5	34727
90/10	32327
85/15	33860
80/20	32872
PLA chip	65180

3.2. Denier of PLA/PHBV fibers

Table 2 shows evaluation of denier of fibers from PLA/PHBV blends of ratio 95/5, 90/10, 85/15 and 80/20 wt% at draw speed of 450-1100-1600, 500-1100-1600 and 550-1100-1600 m/min. PLA shows high denier when increase the draw speed, while the blend did not show significant difference. It was found that

PLA/PHBV of ratio 95/5 and 90/10 showed smaller size of denier more than other. However, the morphology of the blend with ratio 20/80 showed better smooth surface with less phase separation.



Fig. 1. Appearance of PLA/PHBV fibers from melt spinning technique with ratio 80/20 wt%.

Table 2. Denier of PLA/PHBV fibers.

Ratio of PLA/PHBV (wt%)	Denier (dtex)		
	Draw speed of Duo (m/min)		
	450	500	550
PLA	126.21	132.54	133.49
95/5	132.86	132.93	132.96
90/10	129.82	128.66	129.05
85/15	133.59	132.29	134.30
80/20	135.05	132.68	133.59

3.3. Mechanical properties

3.3.1 Tenacity of PLA/PHBV fiber

Table 3 shows tenacity of PLA/PHBV blend fibers at draw speed 450-1100-1600, 500-1100-1600 and 550-1100-1600 m/min. The results show similar tendency of the decreasing of tenacity while increasing the draw speed. The draw speed of 450-1100-1600 m/min shows clearly tenacity of fibers decreased when increasing the amount of PHBV. The immiscibility of PLA and PHBV results in phase separation which might occur from the arrangement of polymer structure in amorphous region. On the other hand, the low draw speed allowed arrangement of polymer structures in the crystalline region. The maximum of tenacity was found with the PLA/PHBV blend with ratio of 95/5 and 90/10 by weight.

Table 3. Tenacity of PLA/PHBV fibers.

Ratio of PLA/PHBV (wt%)	Tenacity (cN/dtex)		
	Draw speed of Duo (m/min)		
	450	500	550
PLA	1.09	1.04	0.90
95/5	1.24	0.93	0.80
90/10	1.09	0.72	0.46
85/15	0.66	0.54	0.59
80/20	0.64	0.62	0.59

3.3.2 Shrinkage of PLA/PHBV fiber

The percent of shrinkage of the fibers after fabrication was evaluated and shows in Table 4. The shrinkage of the fiber was found to be small for the polymer blends when increase the draw speed. It was found that at the draw speed of 500-1100-1600 m/min, the highest of shrinkage PLA occurred. However, the PLA/PHBV blends of ratios 95/5 and 90/10 show small shrinkage, which may due to crosslink of polymer structure.

Table 4. Shrinkage of PLA/PHBV fibers.

Ratio of PLA/PHBV (wt%)	Shrinkage (%)		
	Draw speed of Duo (m/min)		
	450	500	550
PLA	9.3	13.3	4.7
95/5	6.7	5.3	4.3
90/10	10.0	4.3	4.0
85/15	12.0	11.7	11.3
80/20	9.0	8.0	7.7

3.3.3 Sonic Velocity of PLA/PHBV fiber

Table 4 shows the Sonic Velocity of fiber of PLA and PLA:PHBV blends at different draw speed. The results show that the Sonic velocity decreased while increasing draw speed. The stretches of fibers resulted from pulling with high draw speed results in high density. Addition of PHBV to PLA results in decreasing of the value of Sonic velocity. The blends of PLA/PHBV ratio 95/5 and 90/10 showed small decreasing of Sonic velocity than the PLA.

Table 5. Sonic velocity of PLA/PHBV fibers.

Ratio of PLA/PHBV (wt%)	Sonic velocity (%)		
	Draw speed of Duo (m/min)		
	450	500	550
PLA	2.48	2.37	2.28
95/5	2.44	2.37	2.26
90/10	2.30	2.30	2.17
85/15	2.40	2.26	2.07
80/20	2.25	2.21	2.11

3.4. Thermal properties

Thermal analysis was carried out using a differential scanning calorimeter in a nitrogen atmosphere, with a heating rate of 10 °C/min. Two heating cycles were used for each sample evaluation. The samples were first heated from room temperature to 240°C to eliminate their thermal history and then cooled to 30°C and immediately reheated to 240°C. The DSC data of the PHB/PBS blends examined in this work are collected in Table 2. A T_m at 153.79°C for the pure PHBV was found. The T_m for the composition mixture of PHBV and PBS blends were found at 109.33-112.60°C, evidencing that the two polymer phases were separated upon solidification. After reactive blending, the blend of ratio 80/20 showed two peaks of melting temperature, which evidenced the phase. As can be seen that crystallization increased when increasing a composition of PHBV [4].

Table 6. Thermal analysis of PLA/PHBV blends.

Ratio of PLA/PHBV (wt%)	Melting temperature, T_m (°C)		
	Draw speed of Duo (m/min)		
	450	500	550
PLA	162.4	162.6	162.7
95/5	164.1	162.9	163.6
90/10	164.3	164.7	164.9
85/15	164.4	165.3	164.7
80/20	164.8	165.6	164.4

3.5. Preparation of the Knitting Socks

Fig. 2 shows the Socks fabricated from the blends of PLA/PHBV ratios 95/5, 90/10, 85/15 and 80/20 by weight. The polymer blends with all components can be used preparation of the Knitting Socks. However, it was found the most appropriate ratios of PLA/PHBV for the Knitting process are 85/15 and 80/20 by weight. They also showed higher strength. The results confirmed that the above ratios of polymer blends can be applied to textile industrial applications.

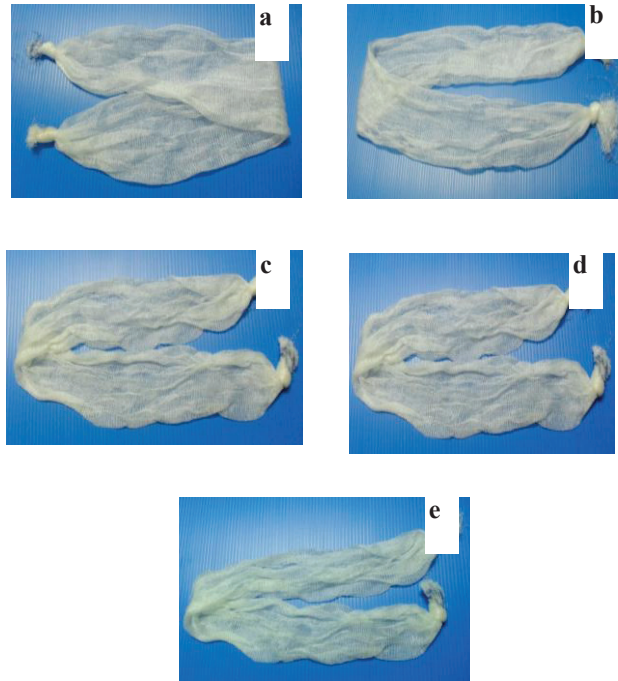


Fig. 2. Knitting Socks from PLA/PHBV blends: (a) 100/0, (b) 95/5, (c) 90/10, (d) 85/15 and (e) 80/20.

3.6. Morphology of PLA/PHBV blends

The morphology of the blends was investigated with high-resolution scanning electron microscopy (SEM), operated at an acceleration voltage of 5 kV. The blends were fractured in liquid nitrogen. The SEM images of the blends are shown in Fig. 3. PLA shows smooth surface (a) while the polymer blends exhibit incompatibility as the amount of PHBV (b) and (c).

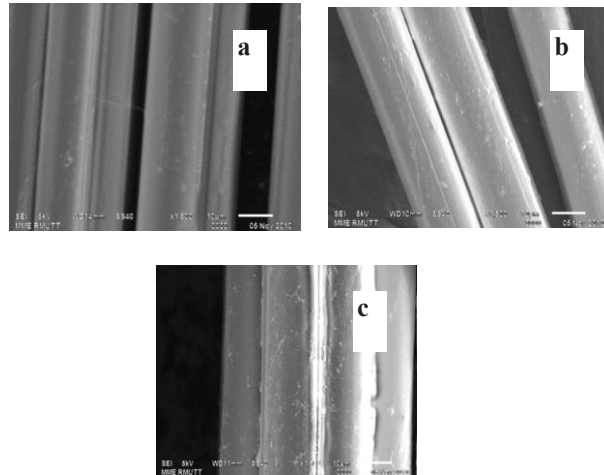


Fig. 3. SEM images of PLA/PHBV blends: (a) 100/0, (b) 95/5, (c) 85/15.

4. Conclusion

Preparation of polymer blends between PLA and PHBV was found to be partial compatible at all ratios. The PLA/PHBV ratio 95:5 exhibited a highest elongation, which is suitable for film blow molding and fiber fabrication application. The fibers from PLA/PHBV blends were prepared using electro spinning process at 450, 500 and 550 m/min of draw speed. The thermal property analysis of polymers showed melting temperature of PLA at 162.7 °C and PLA/PHBV at 164.0°C. The highest Tenacity and shrinkage of polymers were found with PLA/PHBV blends of 95/5 and 90/10. The Sonic velocity of the polymer blends decreased while increasing the draw speed as well as increasing the amount of PHBV. The morphology of all ratio are show partial compatibility at draw speed of 450 m/min. The highest of molecular weight of PLA/PHBV was found with the 95/5 blends at 34727 g/mol at 450 m/min. The fibers form PLA/PHBV blends were subjected to knitting to prepare the Knitting Socks and the blends of ratio of 95/5 and 90/10 produced most suitable products.

Acknowledgements

The authors gratefully acknowledge NIA Research Fund (Project number P-09-00081), Department of Materials and Metallurgical Engineering, Department of Chemical and Materials Engineering, and Department of Textile Engineering, Faculty of Engineering, Rajamangala University of Technology Thanyaburi (RMUTT), Thailand.

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